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Art. I.—*The L absorption limits of Lutecium, Ytterbium, Erbium and Terbium.*

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(Communicated by Professor T. H. Laby.)

[Read 12th March, 1925.]

Summary.

1. The L series absorption wave lengths of Lutecium, Ytterbium, Erbium and Terbium have been measured relative to standard lines.
2. A comparison has been made between the absolute determinations of the wave lengths of the K emission lines of copper and some of the L lines of tungsten.
3. A metal X-ray tube, with a thin window, and capable of operation at 30 kilovolt and 30 milliamperes, has been devised.
4. The values obtained for the absorption limits have been compared with those interpolated by Bohr and Coster. The bearing of these results on the binding energy of electrons in the 5_2 orbit is briefly discussed.

Objects of the Investigation.

To assist in the confirmation of the Bohr atomic theory, experimental evidence regarding the "energy levels" for each element is of importance. The behaviour of the atom as regards energy expresses itself most clearly and most simply in the existence of the absorption limits, and the spectroscopic series terms derived from these serve to determine the atomic states and the energies associated with each. For certain groups of elements, wherein, according to Bohr, an upbuilding of inner uncompleted electron groups takes place, information concerning these limits is especially desirable. At the commencement of this work, no measurements had been published of L series absorption limits of elements in the largest of these groups, that of the rare earths.

The investigation of this region had been delayed by two causes, the difficulty of obtaining samples of rare earths, and the diminution of intensity of the X-ray beam due to absorption in the walls of the tube and the spectrometer system.

This work was made possible by the courtesy of Professor James, of Durham, N.H., and the Welsbach Co. of U.S.A., who placed at the disposal of Professor Laby, of the Natural Philosophy School of this University, samples of four rare earths —Lutecium, Ytterbium, Erbium and Terbium—in an exceedingly

pure state. A water-cooled metal X-ray tube of the Coolidge type giving a high X-ray intensity, closely associated with a low-pressure spectrometer, permitted the spectra being obtained with reasonable exposures. The wave-lengths of the absorption edges were determined with reference to standard lines which were photographed on the same film; any desired standard line could be obtained by incorporating the element emitting it in the target material.

Apparatus.

The metal X-ray tube, a sketch of which is shown in Fig. 1, was designed by Professor Laby, and constructed by Mr. Martin. The main body of the tube (A) was constructed of brass tubing, the cathode (C) could be removed by screwing it out of the tube (B), the junction being made airtight with wax. The target portion was very light, consisting of a hollow copper cylinder (T), supported by the two copper tubes (I) soldered through the brass plate (G). The cathode and target portions were separated by a lamp-glass connected to each with sealing wax. The target face was inclined at an angle of 86° to the axis of the tube, and the ray after leaving the target at almost grazing incidence passed out through the window (W), the brass tube (E) carrying a screw thread for attachment to the spectrometer chamber. The window was of mica .06 mm. thick, supported by a copper disc containing a slot 15 mm. long and 5 mm. wide, and was attached by wax.

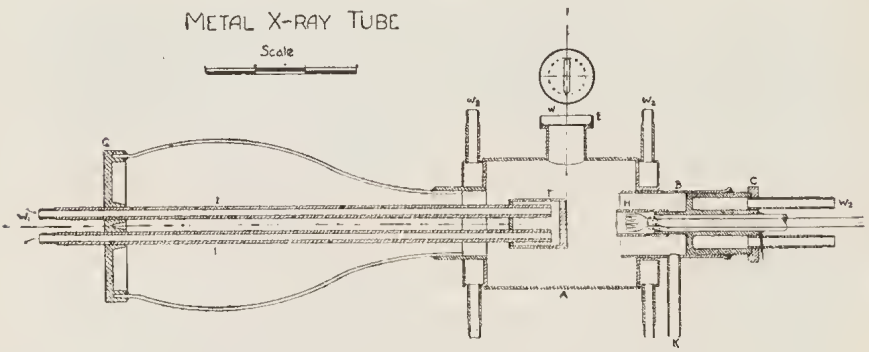

Fig. 1.—Sketch of metal X-ray tube.

The filament was attached to heavy leads passing through an old lamp seal waxed into the Cathode (C), which could readily be removed for the replacement of filaments. The filament hood (H) capable of being screwed backward and forward relative to the filament, served to focus the cathode ray beam on the target. The tube was evacuated through the outlet (K).

A system of water jackets protected the wax joints from the heat generated in the tube, while the target was kept cool by a stream of water passing through the tubes I. As it was impossible to earth either side of the high potential machine, an insulated reservoir as well as an insulated receiver was required for both cathode and anode systems.

The metal X-ray tube possessed one disadvantage. In high vacuum work, considerable difficulty arises owing to the gas which has been absorbed by the glass and metal surfaces being liberated at low pressures. The usual procedure is to expel this gas by a prolonged baking at a high temperature under a low pressure. The number of solder and sealing wax joints in the tube rendered this treatment impossible, but continuous pumping for several days produced an increasingly lower pressure. Later the trouble was to a great extent removed by silver-plating the whole of the metal parts. Once the occluded gas had been removed, the opening of the tube to replace filaments did not cause any difficulty in re-evacuation.

The evacuation of the tube to the degree of vacuum necessary for it to function as a Coolidge tube at first gave considerable trouble. Finally this was accomplished by means of a Cenco oil pump, a Gaede rotary mercury pump and a Langmuir condensation pump in series. The connections between the pumps were made by glass tubing of 15 mm. bore, with short lengths of rubber tubing at junctions to metal. The Langmuir pump was connected to the tube entirely by glass, junctions to metal being effected with wax. Phosphorus pentoxide was used to absorb water vapour, and all portions of the system were thoroughly cleaned and dried before setting up.

Considerable care had to be given to the making of the wax-joints; ordinary commercial sealing wax proved very unsatisfactory, as owing to its coarse grain, small holes appeared on the surface after cooling. The best letter wax gave satisfaction only when the red colour was used, the other colours proving inferior, probably because of the colouring matter present. Later Picein gave excellent results.

The production of the high vacuum was greatly facilitated by the passage of a small discharge current through the tube, such as is used in hardening the usual type of gas tube. During the operation of the tube, the pumps were run continuously.

Two types of filament have been used. During the earlier part of the work, fine tungsten wire was employed. The early filaments had a short life of from 10 to 15 hours; this was probably due to the action of mercury vapour from the Langmuir pump upon the filament (1). The introduction of a glass trap, in which the mercury was condensed, between the tube and the pump greatly minimised this action, and filaments then gave service of upwards of 300 hours.

For reasons mentioned later, a Wehnelt cathode was used in the later part of the work. A Wehnelt filament from a wireless valve was kindly presented by Mr. Foster, of the Western Electric Co., but its use was not practicable owing to the limited electron current obtainable. After several attempts, a filament with much greater electron emission was prepared by coating a platinum wire with a mixture of the oxides of barium and strontium. A very thick coating was obtained which did not disintegrate from the core, and which maintained its full electron emission after 20 hours use.

Both types of filament required prolonged baking at a high temperature to rid them of gas; the latter type especially evolved

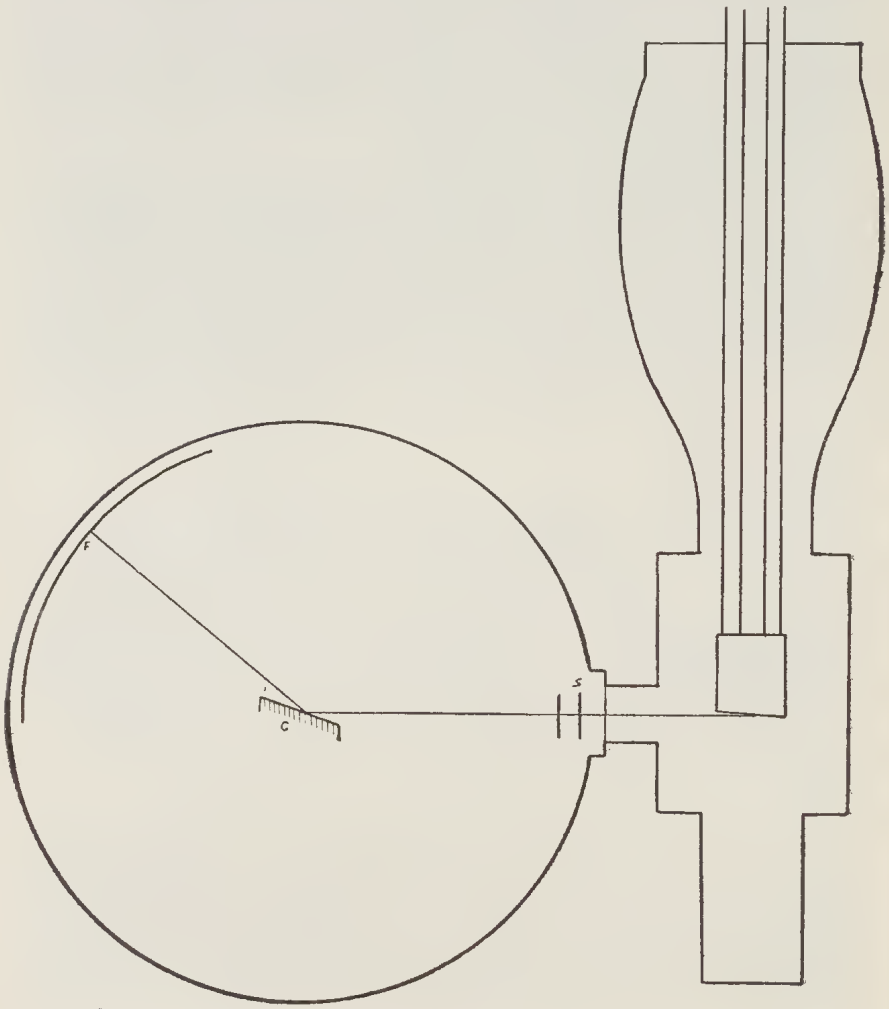

Fig. 2.—Diagram of Tube and Spectrometer.

great quantities during the initial heatings. During this treatment the mercury in both Langmuir and Gaede pumps became contaminated, and required periodical cleaning. After some experimenting, the most satisfactory form of filament was found to be one wound in a small spiral placed at right angles to the axis of the tube. The filament hood was adjusted until the focal spot, as depicted by a pinhole camera photograph taken in line with the slits, showed as a line about 3 mm. long and less than .5 mm. wide. In this way a very intense beam was transmitted through the slit system.

The spectrometer was in essentials similar to that described by Rogers (2), and Martin (3), and only the modifications introduced to suit this work will be mentioned. The crystal table, adapted from a theodolite, was screwed to an iron base plate. The slit system and film holder were carried on iron pillars also screwed to this base. The whole was surrounded by a metal cylinder fitting on the base plate and closed at the top with a sheet of plate glass. The tube was attached to the side of the cylinder (see Fig. 2), so that the window was brought to within 1 cm. of the slits. The attachment of the tube to the spectrometer necessitated that the latter should be insulated from earth by ebonite sheets. The crystal was of Calcite, and was rotated by a shaft passing through a stuffing box in the side of the cylinder and turned by a small motor and reduction gear. The spectrometer was filled with hydrogen at a reduced pressure to reduce the absorption of the rays.

The spectrometer was adjusted in a manner similar to that described by Rogers and by Martin. The focal spot was brought into the line of the slits by setting the crystal at zero, and rotating the tube and chamber on the base plate until an instantaneous photograph showed the crystal to intercept one-half of the beam. As little difficulty was experienced from the wandering of the focal spot, a maximum intensity was thus obtained.

The absorption limits were obtained by passing the general radiation from the tube through the element, and analysing the emergent beam with the spectrometer. The photograph then showed a darkening caused by the continuous radiation of wave-lengths longer than the critically absorbed wave-lengths, ending on the short wave-length side with a sharp edge denoting the limit of absorption.

The maximum current passed through the tube was limited by the heating of the high tension generator (a Snook-Victor transformer and rectifier). The X radiation was excited by a potential of 30 kilovolt, the tube being run continuously at from 25 to 30 milliamperes with the tungsten filament, and from 15 to 20 milliamperes with the Wehnelt Cathode. Currents of more than twice this amount have been passed through the tube for periods of a few minutes. The Copper K radiations were at first chosen as standard lines, but on analysing the beam from the target, strong tungsten L radiations were found due to the deposition of

tungsten from the filament. This provided a second set of reference lines with a greater wave-length range. Three edges (Ytterbium LII, Erbium LIII, and Terbium LI) lay so close to tungsten lines that they could not be distinguished from them. These tungsten lines could not be avoided, since they appeared fairly strongly after an hour's operation of the tube after the insertion of a new target. A Wehnelt Cathode was, therefore, substituted for photographs of these three edges, and the copper lines used as standards.

An absorbing screen of the elements was obtained by spreading a film of Collodion on a clean glass plate, and depositing a small quantity of the earth upon this film. On drying the film and stripping it from the glass, a screen of sufficient thickness was obtained, which produced little absorption of the X-ray beam, other than that due to the characteristic absorption of the element. This screen was fixed on the tube side of the slit.

Photographs of the edges were obtained by a very slow rotation of the crystal over 7 minutes on either side of the edge, and of the reference lines by a short exposure with rapid rotation of the crystal. In cases where an edge was situated close to a reference line, the prolonged exposure in this region resulted in excessive broadening of the reference line; this difficulty was overcome by photographing the reference lines first, and then covering a strip of the film with a copper sheet which prevented further radiation broadening a portion of the reference lines.

To diminish the absorption in the film wrapper, a sheet was made up of tissue paper and aluminium leaf, with a total thickness of .15 mm.; this prevented any action of ordinary light on the film, and absorbed much less radiation than the usual black paper wrapper. "Superspeed" Duplitised X-ray film was used with a rear intensifying screen.

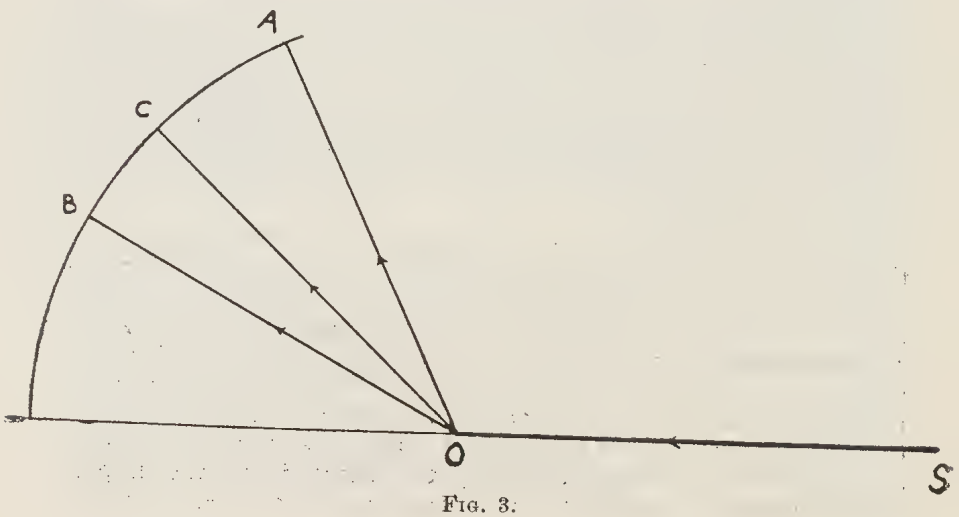

FIG. 3.

The slit width used varied between .075 and .1 mm., with the former the Copper K α doublet (wave-length difference 3.9 X.U.) showed lines on the film distant apart about .16 mm. Exposures of less than 10 minutes were required for the Copper K spectrum; for edges the time varied from 3 to 8 hours with the tungsten filament, and with later improvements and the Wehnelt cathode, from 1 to 4 hours. In general the L_I edge required about 3 times the exposure required for the L_{III}.

Measurement of Films.—The evaluation of the wave-lengths of unknown lines by the reference method can be explained by reference to Fig. 3.

SO is a narrow beam incident upon the crystal face at O. OA, OB represent the paths of two known wave-lengths λ_1, λ_2 reflected at angles θ_1, θ_2 respectively, and OC the path of an unknown wave-length λ_0 reflected at θ_0. If A, C, B be points on a circle with centre O, then $\frac{\text{arc AC}}{\text{arc AB}}=\frac{\theta_1-\theta_0}{\theta_1-\theta_2}$.

If the rays be received on a photographic film bent to form the arc A C B, and the actual distances on the film of AC, AB are X and Y,

$$\frac{X}{Y}=\frac{\text{arc AC}}{\text{arc AB}}=\frac{\theta_1-\theta_0}{\theta_1-\theta_2}, \text{ whence } \theta_0=\theta_1-\frac{X(\theta_1-\theta_2)}{Y}$$

and λ_0 is obtained from the equation $n\lambda=2d\sin\theta$.

The reflection angles for the standard lines have been determined from their wave-lengths, taking "d" for calcite as 3029.04 X.U.

The distances between the lines and edges on the film were measured by a projection method suggested by Professor Laby and developed in this laboratory by Rogers. The film was projected by a lantern on to a vertical screen carried on the platform of a dividing engine; displacements of the platform could be read to .005 mm. The platform was moved until each line in turn was brought to coincide with a fine line on the screen, and the distance read. Magnifications of from 6 to 10 were used, the mean of readings taken at 2 magnifications being taken for each film. By using a high power filament lamp, and varying the current, a clearer definition of the edge could be obtained. The film was then calibrated in seconds per mm. of projection by dividing the angular differences between two standard lines by their distance apart, and the mean taken for values obtained from different pairs of lines. The angle for any unknown line could then be determined from its distance from any standard.

The projection method of film measurement possesses advantages over a microscope micrometer method. Table I. gives a series of displacement measurements. The probable error is shown for the interval $Cu\alpha_1$—$Cu\beta_1$ in which occurs the maximum variation between individual readings. The magnification in this case was about 6.7, so that the probable error for the film proper

was less than .004 mm., which was considerably less than that obtainable by means of a microscope. The corresponding probable error in the wave-lengths is less than .03 X.U. In addition the ability to use both eyes in normal light intensities obviates the strain caused by continuous working with the microscope.

TABLE I.

Specimen of Displacement measurements; Distances in mm. from $Cu\alpha_1$

$Cu\beta_1$	$W\beta_1$	$W\beta_2$	Yb L_1	$W\gamma_1$
33.65 mm.	58.76 mm.	67.20 mm.	81.85 mm.	99.90 mm.
33.63	58.80	67.14	81.82	99.90
33.69	58.79	67.16	81.81	99.94
33.67	58.76	67.18	81.79	99.92
33.70	58.79	67.17	81.79	99.89
means 33.668±.02	58.780	67.170	81.812	99.910

A test of the accuracy of measurements by the relative method, even when a large extrapolation is employed, was made by comparing the absolute values which have been determined for tungsten lines with those obtained by measurement relative to the Copper $K\alpha_1$, $K\beta_2$ lines. Siegbahn (4) has determined these latter very accurately. The means of values of the wave-length derived from at least six films for several tungsten lines, and the probable error, are given in the first column of Table II. The second column gives the results obtained by Duane and Patterson (5) by an ionization chamber method, and the third those due to Siegbahn and Dolejsek (6). At the bottom of the table values for three K lines of nickel found on several films are compared with values given by Hjalmar (7).

The extrapolated values differ from those of Duane and Patterson, and from those of Siegbahn and Dolejsek by little more than the probable error, and by no more than the results of these two differ among themselves, thereby showing that the reference method gives an accuracy comparable with that obtained by an absolute method.

TABLE II.

Comparison of wave-lengths of standard lines. Wave-lengths in X.U. (cm. x 10^{-11}).

Line.	Author.	Duane & Patterson.	Siegbahn and Dolejsek.
Cu α_2	1541.32±.06		1541.22
Cu α_1	1537.30	value assumed	
Cu β_1	1389.33	value assumed	
Cu β_2'	1378.4±.2		1378.0
W α_2	1484.45±.07	1484.4	1484.52
W α_1	1473.5±.1	1473.5	1473.48
W β_4	1298.5±.4	1298.9	1298.78
W β_1	1279.1±.1	1279.3	1279.17
W β_3	1259.9±.5	1260.5	1260.00
W β_2	1241.6±.3	1242.3	1241.91
W γ_1	1095.9±.2	1096.4	1095.53
			Hjalmar
NiK α_2	1658.6		1658.60
NiK α_1	1654.1		1654.67
NiK β_1	1496.7		1496.62

Table III. gives the values obtained for the absorption limits. In only two cases (Ytterbium LII and Terbium LIII) was extrapolation necessary. The values assumed for the tungsten standard lines (α_1,β_1,β_2, and γ_1) were the means of those of Siegbahn and Dolejsek, and of Duane and Patterson, given above. The results are the means of, in most cases, 3 films.

TABLE III.

The L absorption limits of Lutecium, Ytterbium, Terbium and Erbium. Wave-lengths and /R units.

		Wave Lengths. X.U.			ν/R Units.			
		Author.	C.N.W. Cork.		Author.	C.N.W.Cork.		Inter-pol'ted
71	I.	1136.21±.04	1136.2		802.03	802.05		801.1
	II.	1194.0 ±.1	1194.5		763,21	762.87		763.1
Lu	III.	1337.5 ±.2	1337.7		681.32	681.24		681.0
70	I.	1176.4 ±.1	1176.5	1171	774.65	774.55	778.2	773.4
	II.	1238.14±.05		1242	735.85		733.7	735.7
Yb	III.	1382.64±.03	1382.4	1386	659.10	659.20	657.5	659.6
68	I.	1265.5 ±.1	1266.0	1265	720.08	719.78	720.4	718.1
	II.	1335.60±.1	1335.3	1336	682.29	682.45	682.1	682.8
Er	III.	1479.19±.03	1479.6	1478	616.05	615.85	616.0	616.5
65	I.	1417.0 ±.2			643.10			642.4
	II.	1499.4 ±.1			607.75			608.2
Tb	III.	1644.2 ±.1			554.24			553.8

Since the commencement of this work, determinations of the wave-lengths of some of the rare earths have been made by Coster, Nishini and Werner (8), and by Cork (9). Their values for the elements done here are shown for comparison, as well as values of ν/R. The last column contains values of ν/R interpolated by Bohr and Coster (10).

The edges obtained showed two characteristics, in some places, a pronounced "edge" was found, with an interval on the short wave-length side, where a great proportion of the radiation had been absorbed, in others an absorption "line" appeared as a light line on a dark background.

This phenomenon has been noticed by Coster, Nishini and Werner, and by Siegbahn (11), and the appearance of the line or edge was thought to be dependent upon the thickness of the absorbing layer of the element. Owing to the inequalities of thickness in the absorbing layers used in my experiments, in some cases both "line" and "edge" appeared on the same film. The line breadth approximated to that of the breadth of slit, and values of the critical absorption wave-length obtained by measuring to the centre of the line and to the edge showed a discrepancy until a correction corresponding to half the slit width, was applied in the case of the edge values.

The values obtained in this experiment for the absorption wave-lengths agree well with those of Coster, Nishini and Werner; the possible error given by these workers is 0.5X.U, and in no case is the disagreement between their results and mine greater than this. In the case of Erbium, these workers give as reflection angle for the L$_{II}$ edge as 12°44′0″, the wave-length as 1334.9 X.U. and ν/R units as 682.62; but on substitution of this angle for reflection, however, a wave-length of 1335.3 X.U. and a ν/R unit of 682.45 is obtained, and these corrected values have been used in this table.

The values due to Cork show large unsystematic deviations which are probably due to large limits of error. In two cases, edges measured by him lie very close to strong tungsten lines, due to that metal being used as target in his tube. The writer found it impossible to distinguish between the Erbium L$_{III}$ edge 1479 X.U. and the tungsten α doublet at 1473 X.U. and 1484 X.U., and between Ytterbium L$_{II}$ 1238 X.U. and tungsten β_1, 1241 X.U. It would appear that the spreading of the strong lines after exposures of 30 to 40 hours (as used by Cork) would confuse the edge lying close to them.

Comparison between the different ν/R values proves interesting. The interpolated values of Bohr and Coster are interpolated from values determined for elements from N=92 to N=74 and from N=60 to N=55. In the case of the values for the L$_{II}$ and L$_{III}$ limits, the observed values show an unsystematic variation slightly larger than the probable errors. In the values for the L$_I$ limit, however, a systematic deviation of several times the probable error occurs, as is shown in Table IV. and Fig. 4. The probable

error in ν/R units in the value of Coster, Nishini, and Werner is less than .25, and in the writer's values less than .1. In Fig. 4, the deviations noticed by Coster, Nishini and Werner and by the writer have been plotted against the atomic number.

TABLE IV.

Deviations in ν/R units from the interpolated values.

Atomic Number.	L I. Author.	L I. C.N.W.	L II. Author.	L II. C.N.W.	L III. Author.	L III. C.N.W.
71	.9	.9	.1	—.2	.3	.2
70	1.2	1.2	.2		—.5	—.4
68	1.9	1.7	—.5	—.4	—.4	—.7
65	.7		—.5		.4	
58		.3				

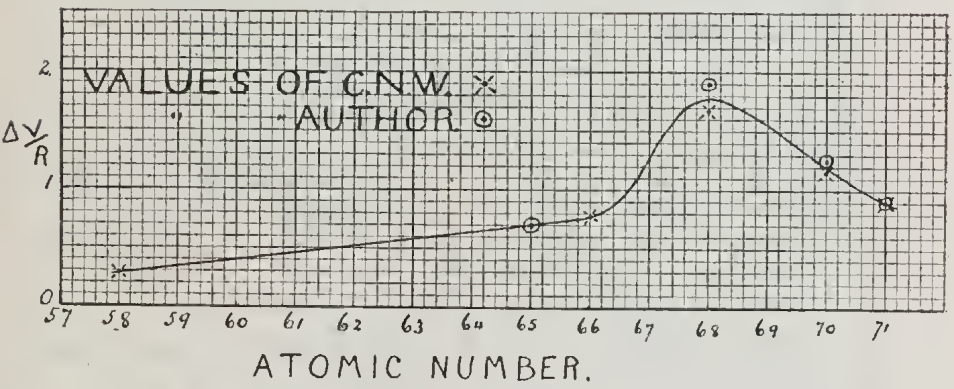

FIG. 4.—Graph of deviations in $\frac{\nu_l}{R}$ units from the interpolated values.

It will appear that the interpolated values of L_I from N=71 to 65 differ from the observed values, and that this deviation has become within the limits of error by the time Cerium (58) is reached.

In providing for the increase of the number of electrons with increasing atomic number, Bohr conceives of four periods of elements wherein electrons are placed in inner orbits after outer orbits have been commenced. In the cases of the iron, palladium, and platinum groups, however, no shell with a higher quantum number than the shell being built up, has reached a stage of completion. For the rare earths group, the O-shell has reached a stage of completion in that it contains two groups of 4 electrons each (the 5_1 and the 5_2 orbits) by the time that Xenon (N=54) is reached. Subsequent increase in the atomic number expands 3 groups, (the 4_1, 4_2, and 4_3 orbits) from 6 electrons each to 8, and a fourth group (the 4_4 orbit) is added. Some irregularities might then be expected.

It appears that the ν/R values for the L_I level arrived at by interpolation are too low, and that a sharp kink in the graph of ν/R against atomic number for this level occurs in the region of the rare earths. Since the energy difference between the outside of the atom and the 5_2 orbit was obtained by Bohr and Coster from the frequency difference between the interpolated values for the L_I edge and the observed frequency of the $L\gamma_4$ line, an increase in the values for the L_I edges would imply an increase of nearly 50 per cent. in the values (vide Bohr and Coster), formerly associated with the 5_2 orbit, and that the binding of electrons in this orbit may be appreciably greater than that of valency electrons.

This work was carried out while the writer was a Fred Knight and University Research Scholar. I wish to thank Professor Laby for his suggestion of this work, and for his valuable advice and interest during its progress. Thanks are also due to Professor James and the Welsbach Co. for their generosity in providing the rare earth samples.

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